PB80-162217

Arsenic: A Preliminary Materials Balance

Lowenbach and Schlesinger Associates, Inc.
McLean, VA

Prepared for

Environmental Protection Agency
Washington, DC

Mar 79

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of
Toxic Substances
Washington, D.C.

March 1979
EPA-560/6-79-005

Toxic Substances

PB80-162217

EPA

Arsenic:

A Preliminary Materials Balance

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-560/6-79-005		PB 80 162217

4. TITLE AND SUBTITLE	5. REPORT DATE
ARSENIC: A Preliminary Materials Balance	March 1979
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
William A. Lowenbach and Joyce S. Schlesinger	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Lowenbach and Schlesinger Associates, Inc. 1842 Kirby Road McLean, Virginia 22101	11. CONTRACT/GRANT NO. Purchase Order No. W-1434-NNSX
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Protection Agency Office of Toxic Substances 401 M Street, S.W., Washington, D.C. 20460	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Existing data on the natural and anthropogenic sources of arsenic emissions are compiled and presented in a fully annotated tabular format. Arsenic distribution in the environment is graphically displayed in terms of air, land, and water emissions. Fossil fuel consumption for energy production, arsenic production and commercial use, and primary copper smelting are identified as the three major sources of environmental emissions. Data gaps are identified and recommendations for further study outlined.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Arsenic, sources of emissions		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
unlimited	unclassified	
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

☆ U.S. GOVERNMENT PRINTING OFFICE 1979 -281-147/36

ARSENIC: A PRELIMINARY MATERIALS BALANCE

Prepared by:

Lowenbach and Schlesinger Associates, Inc.
1842 Kirby Road
McLean, Virginia 22101

Purchase Order Number: W-1434-NNSX

Project Officer
Dr. C. Richard Cothern

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C. 20460

This report has been reviewed by the Office of Toxic Substances, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Existing data on the natural and anthropogenic sources of arsenic emissions are compiled and presented in a fully annotated tabular format. Arsenic distribution ot the environment is graphically displayed in terms of air, land, and water emissions. The three major sources of arsenic to the environment are identified as fossil fuel consumption for energy production, arsenic production and commercial use, and primary copper smelting. Data gaps are identified and recommendations for further study outlined.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
LIST OF FIGURES	v
LIST OF TABLES	vi
EXECUTIVE SUMMARY	vii
I. INTRODUCTION	1
Project Objective	1
Scope of Work	1
II. ARSENIC MATERIAL BALANCES	3
Data Collection and Presentation	3
Problem Areas	4
Arsenic Emissions	8
III. SUMMARY AND CONCLUSIONS	50
REFERENCES	53

LIST OF FIGURES

Number		Page
1.	Distribution of Arsenic Emissions to the Atmosphere	5
2.	Distribution of Land-Disposed Arsenic Wastes	6
3.	Distribution of Arsenic Wastes Discharged to Surface Waters	7

LIST OF TABLES

Number		Page
I	Arsenic Emissions: Natural Sources, metric tons per year	9
II	Arsenic Emissions: Arsenic Production and Use, metric tons per year	12
III	Arsenic Emissions: Energy Production, metric tons per year	17
IV	Arsenic Emissions: Concentrations of Arsenic in Fuels and Waste Products	21
V	Arsenic Emissions: Primary Copper Smelting, metric tons per year	24
VI	Arsenic Emissions: Copper Refining, metric tons per year	30
VII	Arsenic Emissions: Primary Lead and Zinc Industries, metric tons per year	33
VIII	Arsenic Emissions: Primary Non-Ferrous Metal Ores Mining and Milling, metric tons per year	36
IX	Arsenic Emissions: Manganese Production, metric tons per year	39
X	Arsenic Emissions: Iron Ore Production and Steelmaking, metric tons per year	41
XI	Arsenic Emissions: Phosphorus Production, metric tons per year	44
XII	Arsenic Emissions: Boron Production, metric tons per year	47
XIII	Arsenic Emissions: Water and Wastewater Treatment, metric tons per year	49

EXECUTIVE SUMMARY

As a first step in assessing the risk presented by arsenic and its compounds, the U.S. Environmental Protection Agency, Office of Toxic Substances has undertaken a review of arsenic emissions from natural and anthropogenic sources. This study discusses the distribution of arsenic in the United States within the confines of a material balance, identifying arsenic input, that which is dispersed to air, land, and water, and that which is contained.

Arsenic ranks 20th among other elements in crustal abundance and is a constituent of an estimated 245 mineral species. Sulfide deposits associated with nonferrous ores have elevated arsenic concentrations, as well as sedimentary deposits such as iron ore, phosphate rock, borax ore, manganese ore, and fossil fuels. Arsenic is commercially produced as a by-product of the ASARCo-Tacoma primary copper smelter.

Processing of raw materials, such as nonferrous ores, and fossil fuels, results in the release of arsenic to the environment. Other man-made sources of arsenic emissions include its use in the manufacture of commercial products, such as arsenical pesticides, or as a product additive (e.g., lead alloy industry).

Arsenic emissions to air, land, and water are summarized in Figures 1, 2, and 3. In terms of arsenic released per year, energy production represents the largest single source of arsenic discharged to the atmosphere and the second largest source (pesticide application is larger) of discharges to land. Primary copper smelting is the third major source of arsenic emissions to the environment.

The conclusions reached in this study are based, nonetheless, on a cursory review of existing arsenic emissions data. Because the majority of this information is unsubstantiated, and in many cases limited to the author's "best guess", a summary table totaling arsenic emissions to all three sinks has been deliberately omitted. Instead, the origin of each piece of data is discussed

within the tabular format of the report. Recommendations for further data collection and evaluation are outlined, highlighting existing data gaps.

SECTION I

INTRODUCTION

PROJECT OBJECTIVE

Arsenic is a recognized toxic substance and suspected occupational carcinogen that has recently been placed under scrutiny by Federal regulatory agencies. As an initial step in assessing the risk presented by arsenic and arsenic compounds, the U.S. Environmental Protection Agency, Office of Toxic Substances, has begun a review of potential sources of arsenic exposure. The purpose of this study is to address the distribution of arsenic to the environment.

SCOPE OF WORK

The scope of this report has been limited to a review of published data concerning the flow of arsenic within the United States. Available literature has been critiqued and compiled in a single document with the intention of presenting (1) an overview of major sources of arsenic emissions, (2) fully annotated tables to aid data evaluation, and (3) an indication of data gaps. While many primary sources were searched during the literature review, no attempt was made to generate new data points or estimate emission factors. Furthermore, no attempt was made to include a discussion of the fate and transport of arsenic within each of the three environmental sinks: air, land, and water.

Data collection, sources of information, and problem areas are reviewed in Section II. Existing data (with introductory prefaces) are presented in a tabular format for the following categories:

- Natural Sources
- Arsenic Production and Use
- Energy Production
- Concentration of Arsenic in Fuels and Waste Products
- Primary Copper Smelting
- Copper Refining
- Primary Lead and Zinc Industries
- Primary Non-Ferrous Metal Ores Mining and Milling
- Iron Ore Production and Steelmaking
- Phosphorus Production
- Boron Production
- Water and Wastewater Treatment

Finally, Section III presents major conclusions, including recommendations for future studies.

SECTION II

ARSENIC MATERIAL BALANCES

DATA COLLECTION AND PRESENTATION

The purpose of this study was to compile the available data on arsenic input and emissions from natural and cultural sources. The tabular format chosen, with extensive use of footnotes, serves to highlight data gaps, unsubstantiated estimates of emission factors, and conflicting data points, while providing a comprehensive summary of the available information. In preparing the arsenic material balance for the United States, the following literature served as primary sources of data:

National Inventory of Sources and Emissions:
Arsenic - 1968
W. E. Davis & Associates, 1971.

Technical and Microeconomic Analysis:
Arsenic and its Compounds
U.S. Environmental Protection Agency, 1976.

Emission Factors for Trace Substances
Anderson, D., 1973.

Medical and Biological Effects of Environmental Pollutants: Arsenic
National Academy of Sciences (NAS), 1977.

Gross Annual Discharge to the Waters in 1976:
Arsenic U. S. Environmental Protection Agency, 1978.

Preliminary Draft: Environmental Assessment of Arsenic Emissions from Primary Copper Smelters*
U.S. Environmental Protection Agency, 1979.

---

* This report has not been formally released by the Agency. An updated draft of Chapter 3, Appendix F, and Table 4-6 "Summary of Fugitive Arsenic Emissions at Primary Copper Smelters under Existing Control" were forwarded to J. Schlesinger by A. Vervaert for use in this document.

Secondary sources of data included:

- A search of Chemical Abstracts for the preceding twelve year period;
- Information in the priority pollutant file maintained by the Water Quality Analysis Branch, Office of Water and Waste Management;
- Personal interviews with representatives of EPA (IERL, OAQPS, OEMI, Water Quality, Effluent Guidelines, and ERL), TVA, and the USGS.

Although informal discussions with EPA personnel and various researchers have provided useful background data, as well as leads to ongoing research/monitoring studies, unpublished data were omitted from this report.

PROBLEM AREAS

Before presenting the compiled data, it is important to consider the problem areas inherent to a study of this nature. First and foremost, total emissions for any one category can be quite misleading, as non-quantifiable emissions are necessarily omitted (i.e., a blank does not indicate zero emissions, but rather, a gap in information). Secondly, it appears that many of the emission factors reported by Davis (1971), EPA(1976a), NAS(1977), and Anderson (1973) are unsubstantiated, and in some cases, quite outdated with regard to existing environmental controls. Furthermore, in some cases, emissions factors cited from primary sources were incorrectly applied to current production data. In other instances, emissions data are based on feed concentrations arbitrarily selected or analogies to other chemicals and similar industrial processes (for lack of better information). Thus, the majority of existing data has not been verified by sampling and analysis and appears to be little more than "engineering judgment or an educated guess".

A summary sheet reporting total arsenic emissions to each environmental sink by category has been deliberately omitted. Instead, in an effort to direct attention to data trends, rather than to "significant figures", total emissions to air, land, and water are graphically presented in Figures 1, 2, and 3, respectively. Numbers that do appear in the Tables, in general, must be regarded as speculative and used with extreme caution. Finally, all data points have been rounded to two significant figures; greater accuracy and precision, based on available information, is unwarranted.

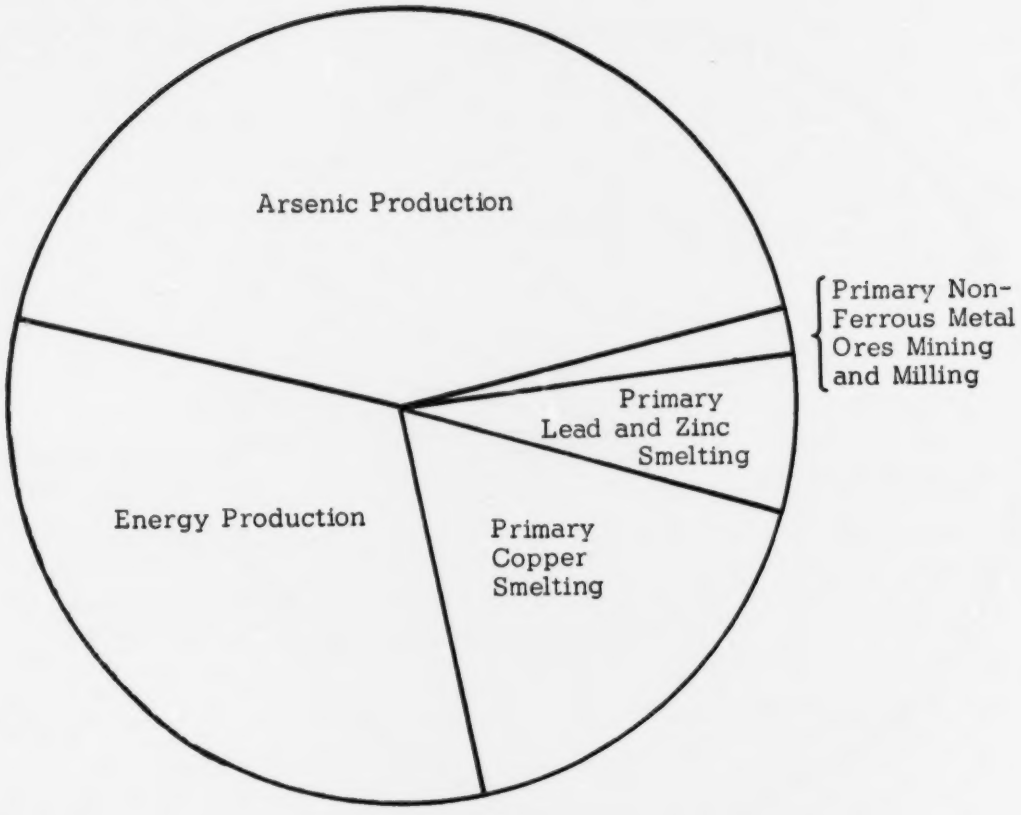

FIGURE 1.

Arsenic Emissions to the Atmosphere

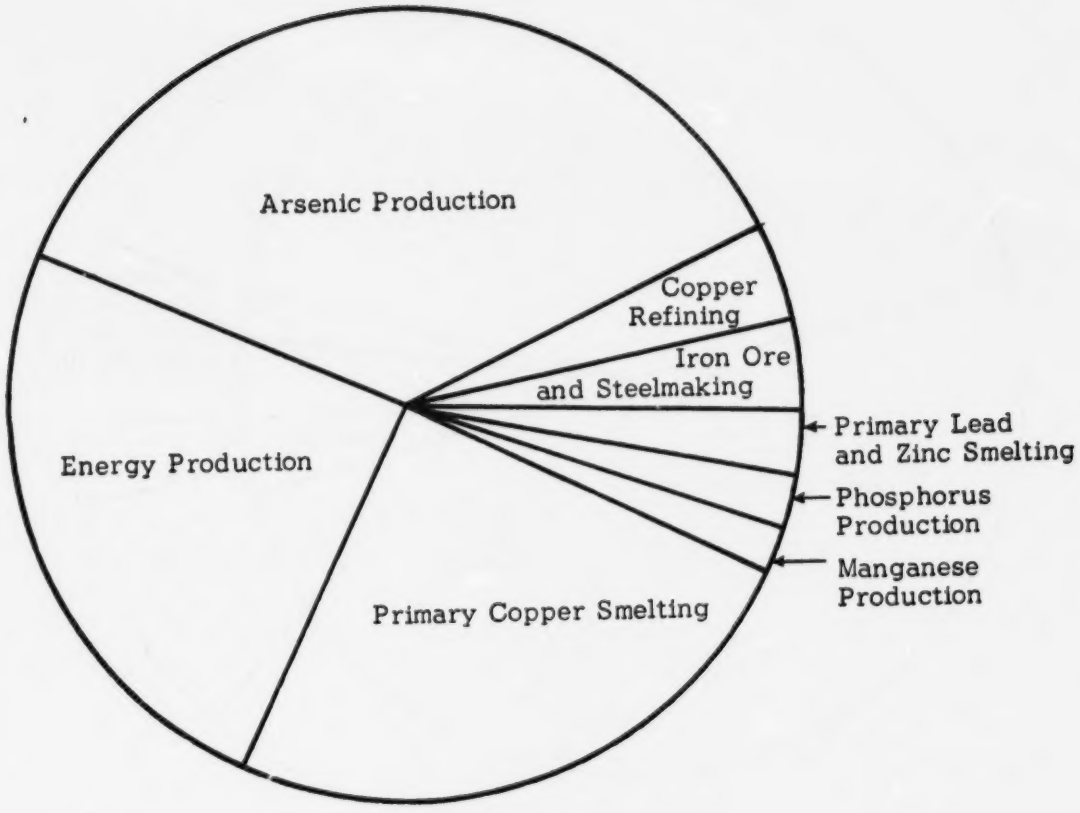

FIGURE 2.

Land-Disposed Arsenic Wastes

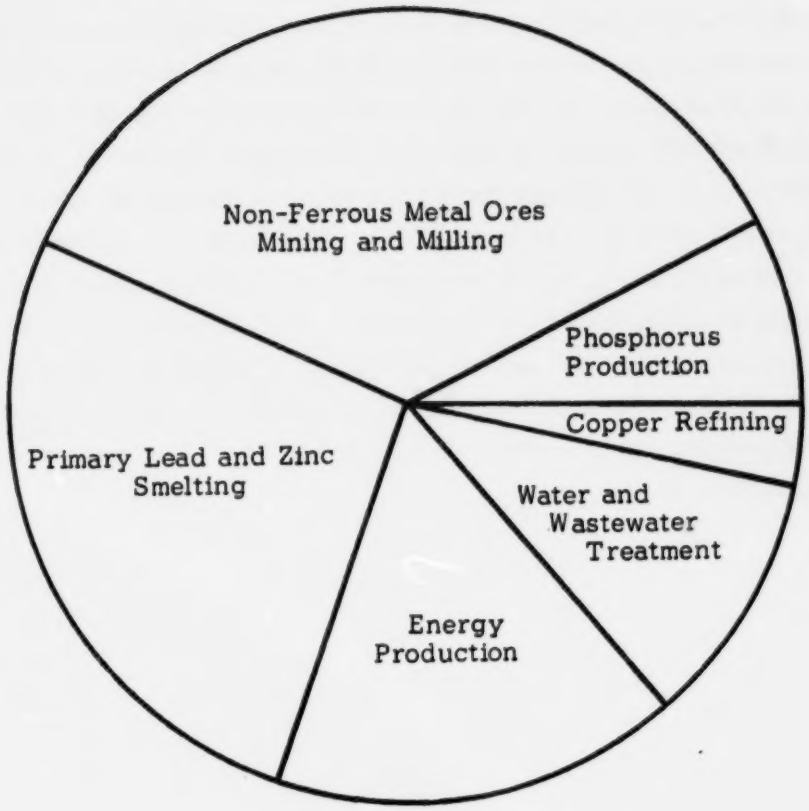

FIGURE 3.

Arsenic Wastes Discharged to Surface Waters

NATURAL SOURCES

Arsenic ranks 20th among elements in crustal abundance, and is a constituent of an estimated 245 mineral species (NAS, 1977). Natural input to the environment may be described in terms of weathering of continental rocks (erosion), as the contribution from volcanic activity is small. (Removal of arsenic from global cycling by sedimentation has not been addressed.) Estimated arsenic emissions from natural sources are shown in Table I and are based on an estimate of the total amount of weathered material transported to the oceans annually (Judson, 1968). The total arsenic input was calculated through (1) gross estimates of the igneous rock, shale, limestone, and sandstone content of the weathered material, and (2) the average value of the arsenic content of each type of rock. If erosion resulting from intensive land use is included in such calculations, the estimated arsenic input from weathering increases from 45,000 to 120,000 metric tons per year (Ferguson and Gavis, 1972).

TABLE I

ARSENIC EMISSIONS: Natural Sources, metric tons per year[1]

SOURCE	INPUT		DISPERSION		
			Air	Land	Water
Weathering[2,3]					45,000 120,000
Igneous Rock	3,000[4]	4,200[5]			3,000
Shales and deep sea sediments	40,000[6]	85,000[7]			40,000
Sandstone and limestone	2,000[8]	2,500[9]			2,000
Volcanic activity[10]					

1. Based on a global arsenic cycle for natural imput. All data are reported to two significant figures and rounded to 5kkg increments.

2. Ferguson and Gavis, 1972. Based on Judsons's (1968) global estimate that 9.3×10^9 metric tons of material are weathered and transported to the oceans annually. Furthermore, it is presumed (see: Conway, 1942) that the weathered material is approximately 20 percent igneous rock, 65 percent shale, and 15 percent limestone and sandstone with respective arsenic contents of 1.8 mg/kg, 6.6 mg/kg, and 1.5 mg/kg.

3. Ferguson and Gavis, 1972. Due to rapid erosion caused by intensive land use, Judson (1968) estimated that the mass of material transported to the oceans has increased to 24×10^9 metric tons/yr, resulting in a proportional increase in the release of arsenic to 120,000 metric tons/yr.

4. Ferguson and Gavis, 1972. Based on reported values of 1.8 mg/kg (Taylor, 1964) and about 2 mg/kg (Onishi and Sandell, 1955).

5. NAS, 1977. Reported as average arsenic concentration in igneous rocks from data provided by Onishi (1969) and Boyle and Jonasson (1973).

6. Ferguson and Gavis, 1972. Based on a reported value of 6.6 mg/kg (Vinogrodow, 1960) for shale.

7. NAS, 1977. Reported (14.5 mg/kg) average arsenic concentration for shales and clays from data provided by Onishi (1969) and Boyle and Jonasson (1973). One sample with an arsenic concentration of 490 mg/kg was excluded from the calculation.

8. Ferguson and Gavis, 1972. Based on a reported value of 1.5 mg/kg (Onishi and Sandell, 1955).

9. NAS, 1977. Based on an average of arsenic concentrations in limestone (1.7 mg/kg and sandstone (2.0 mg/kg).

10. Ferguson and Gavis, 1972. Although the contribution of vulcanism to the arsenic cycle over geological time is recognized to be large, annually, this contribution is suggested to be small in comparison to weathering of continental rocks.

ARSENIC PRODUCTION

The production and uses of arsenic are summarized in Table II. Because there is only one domestic manufacturer of arsenic trioxide (ASARCo-Tacoma, Washington), production data are considered confidential*. The annual production level shown is based upon a material balance estimated by ASARCo and an assumed production time of 8,000 hours; accordingly this figure should be regarded as a gross estimate. Import data are from the Minerals Yearbook, 1975.

The major use of arsenic is pesticide manufacture, followed by fungicide manufacture (principally wood preservatives), glass manufacture, non-ferrous alloying, and feed additive manufacture. Data concerning these uses, like arsenic production, are considered confidential. The figures presented have been compiled from industry estimates and the limited data that are available. Again, these figures can only be regarded as rough estimates.

It is worth noting that demand for many of the uses of arsenic are reported to be in decline (EPA, 1976a). This is particularly true of arsenical pesticides and herbicides with exception of arsenic acid which is used for desiccation of cotton in the Southwestern United States. Arsenic use during glass manufacture is reported as being largely replaced by non-arsenical sulfates.

---

* When there are three or less manufacturers of a particular chemical, combined production data could reveal proprietary information and thus may not be revealed publically.

TABLE II

ARSENIC EMISSIONS: Arsenic Production and Use, metric tons per year[1]

SOURCE	PRODUCTION		DISPERSION				
	Input	Contained	Air		Land		Water
Production[2]	12,000		250				
Imports[3]	9,400						
Total	21,000						
Use							
Pesticides			3,400[6]	2,700[7]	12,000	10,000	-[8]
Production	15,000[4]	13,000[5]	150	130			
Application			2,900	2,200			
Ginning Wastes			20				
Incineration			330[7]	330			
Fungicides	2,000	2,000	neg		neg		neg[9]
Plastics[9]	5						
Wood[10]	2,000						
Alloys[11]							
Brass	10[12]	10	neg				
Copper	100[13]	100	neg				
Lead	950[14]	950	500	500	60		
Gallium Arsenide[15]							
Glass[5]	1,800	1,600	210				
Catalysts[15]							
Feed Additives[16]	410	410	neg				
Miscellaneous[17]							
Total	20,000	18,000	5,100	4,100	3,200	12,000	10,000

1. Data are reported to two significant figures and are rounded to 5kkg increments; emissions below 3kkg are considered to be negligible.

2. EPA, 1979. Data is taken from material balance around ASARCo Plant, Takoma, Washington, 1978. Based on 1,500kg/hr, 8,000 hours per year.

3. Minerals Yearbook, 1975. Bureau of Mines, 1977.

4. EPA, 1976b. 14,800 metric tons/yr of arsenic were estimated to be used for arsenical persticides in 1974. Herbicides: cacodylic acid, disodium methane arsenate hexahydrate, monosodium acid methane arsenate, and arsenic acid. Insecticides: calcium arsenate and lead arsenate.

5. EPA, 1976a. Statement to OSHA by Crosby F. Baker for ASARCo: In Re: PROPOSED STANDARD for Occupational Exposure to Inorganic Arsenic.

6. EPA, 1976b. Air emissions include: organic pesticide application - 2,485 metric tons/yr; inorganic pesticide application - 399 metric tons/yr; incineration of cotton ginning waste - 17 metric tons/yr; production losses from manufacture of arsenical pesticides - 154 metric tons/yr. All based on 1974 emissions.

7. W. E. Davis and Associates (1971). The emission factor for production loss is reported as 0.01; the emission factor for application is reported as 0.168. Based upon 1974 production of 11,540,100 bales of cotton. 0.317 metric tons of trash are produced per bale of cotton of which 37 percent is burned. The arsenic concentration of this waste is assumed to be the same as that of particulate emission during ginning operations (300 mg/kg). 76.6 percent of the arsenic present is lost during combustion for a total emission of 310 metric tons. Ginning particulate emissions are reported as 11.7 lbs/bale of cotton ginned with an average arsenic concentration of 300 mg/kg for a total emission of 18 metric tons.

8. EPA, 1976c. No discharge of wastewaters due to reuse and recycle of all process wastewaters.

9. EPA, 1976a. Principally 10,10' - oxybishpenoxarsine, $C_{24}H_{16}As_2O_3$.

10. Ernst and Ernst 1976. Preservatives include Fluor-chrome-arsenate phenol - 100 metric tons/yr; chromated copper arsenate - type A - 185 metric tons/yr, type B - 849 metric tons/yr, type C - 830 metric tons/yr.

11. EPA, 1976a. Use of arsenic in non-ferrous alloys during 1974 has been estimated at 1,240 metric tons by an ASARCo spokesman.

12. EPA,1976a. Admiralty brass contains 300 mg/kg of arsenic. The total demand in 1968 for all industrial non-electrical copper was 250,000 metric tons. Assuming that 25,000 metric tons (10%) represents an upper limit of admiralty brass production, arsenic use is 7.5 metric tons.

13. EPA,1976a. Copper containing 0.3% arsenic is used in car radiators. A typical car radiator contins 5.9kg of copper. A production level of 10 million vehicles per year thus requires 59,000 metric tons of copper togther with 175 metric tons of arsenic. Such copper is extensively recycled, either by fire refining (which does not remove arsenic) or by electrolytic refining (which removes arsenic as a sludge). An arbitrary estimate of the disposition of the 175 metric tons of arsenic presumed to be present in arsenic scrap is that 75 metric tons is reused in auto readiators (along with 100 metric tons of new replacement arsenic) while 100 metric tons is dissipated in other copper alloys or removed during electrolytic refining.

14. EPA, 1976a. Use of arsenic in lead shot is estimated at 60 metric tons by the Lead Industries Association. Use of arsenic in bearing metals is based on new lead usage of 2,100 metric tons; bearing metals contain approximately 83% lead and 0.6% arsenic. Thus consumption for this use is estimated to be 15 metric tons. Use of arsenic in antimonal lead is estimated as follows: lead consumption for antimonial lead is approximately 350,000 metric tons (of which 6,800 metric tons is primary antimonial lead and 320,000 metric tons are recycled antimonial lead scrap); assuming an overage arsenic concentration of 0.25%, 870 metric tons of arsenic are contained in antimonial lead much of which is lost to the atmosphere during recovery in lead blast furnaces. Using an air emission factor of 0.4 kg/kkg of lead together with the quantity of slag generated from secondary lead blast furnaces (150,000 kkg) at an arsenic concentration of 0.2%, 375 kkg of arsenic is retained in the secondary lead. Thus, by difference, 500 kkg of arsenic must be added.

15. Production figures are unavailable.

16. EPA, 1976a. Emission factor presumed to be one-half that of pesticides (0.01), i.e., 0.005.

ENERGY PRODUCTION

Arsenic emissions to the environment from energy production are summarized in Table III. In terms of amounts discharged per year, energy production represents the largest single source of arsenic discharges to the atmosphere and the second largest source (pesticide application is larger) of discharges to land.

For electricity generation in 1974, 54% of the fuel consumed was bituminous coal, 0.25% anthracite, 1.3% lignite, 23% natural gas, 19% residual oil, and 2.9% distillate oil (Slater and Hall, 1977). The bituminous coal category includes 10 to 15% of subbituminous coal. Included in the natural gas category are less than 0.6% combined coke oven gas, refinery gas, and blast furnace gas. The use of liquified natural gas, synthetic natural gas*, and oil derived from oil shale was, and remains, zero. The residual oil category includes all heavy oils and consists of 0.6% No. 4, 1.5% No. 5, 95.5% No. 6, and 2.4% crude. Distillate oil consisted primarily of No. 2 fuel oil and less than 10% kerosene and jet fuel. Approximately 96% of the consumed fuels were burned in external combustion systems and 4% in internal combustion systems.

Arsenic input and discharges are calculated on the basis of reported arsenic concentrations of fuels and from fuel consumption data. Emissions from coal are much greater than those from petroleum or natural gas because arsenic concentrations are greatest in coal; in fact, no trace elements are present in appreciable amounts in gaseous hydrocarbons.

The arsenic concentration of coal varies widely. Ruch, et al. (1974), in analyzing 101 coals, found arsenic concentrations to range from 0.50 mg/kg to 93.0 mg/kg; an arithmetic mean of 14.02 was reported but means little as the standard deviation of this data was approximately 17 mg/kg. Of the coals analyzed, 82 were from the Illinois Basin, 11 from the Eastern United States, and 8 from Western states. A majority of coals in this study (69 samples)

---

* Coal gasification may lead to significant arsenic emissions however; approximately 25% of the arsenic initially present in the coal is found in the product gas, while the balance remains with the coal ash (Attari, 1973).

contained arsenic in concentrations less than 12 mg/kg. Other arsenic concentrations have been reported as summarized in Table XII. Davis (1971), Anderson (1973), and EPA (1976a) all report an average arsenic concentration in coal of 5.44 mg/kg. According to Anderson (1973), this number is based upon the analysis of a single sample of coal. A value of 28.0 mg/kg for arsenic concentration in coal is reported by Slater and Hall (1977) based upon regional coal usage.

Because of the variation of arsenic concentrations in coal, three estimates of the amount of arsenic present in coal are presented in Table IV. All numbers can only be regarded as providing gross estimates of arsenic emissions occuring during coal combustion. The same statement is also probably true for other fuels but because of lower arsenic concentrations, these emissions are of less concern.

TABLE III

ARSENIC EMISSIONS: Energy Production, metric tons per year[1]

SOURCE	PRODUCTION Input			DISPERSION Air	Land	Water
Production[2]						
Coal						
Bituminous	14,000	6,900	2,700	neg[3]	-	95[4]
Anthracite	50					
Petroleum						
Residual						
Distillate						
Electricity Generation						
External Combustion[5]						
Coal (Total)	11,000[6]		2,500[7]	2,700 650[8]	8,300	150[9]
Bituminous[10]				2,700		
Pulverized dry				2,000		
Pulverized wet				370		
Cyclone				370		
All stokers				20		
Anthracite[11]	15			3	10	
Pulverized dry				neg		
Pulverized wet				-		
Cyclone				-		
All stokers				neg		

(Continued)

TABLE III

SOURCE	PRODUCTION			DISPERSION		
	Input			Air	Land	Water
Petroleum (Total)		20		20		
Residual Oil[12]				20		
Tangential				10		
All other		neg		neg		
Distillate Oil[13]						
Internal Combustion (All)[14]		neg		neg		
Steam and Other[2]						
Coal	4,100	2,100	800			
Bituminous						
Deliveries to consumers	230	110	45			
Manufacturing and mining industries	1,500	730	290			
Steel mills	160	80	30			
Oven coke plants	2,200	1,100	440			
Beehive coke plants	35	15	5			
Bunker	neg	neg	neg			
Anthracite						
Heating	25					
Steel mills	5					
Other	5					
Petroleum						
Residual						
Distillate						

1. Slater and Hall (1977). Data are reported to two significant figures and rounded to 5kkg increments; emissions below 3kkg are listed as negligible.

2. Production figures are from Minerals Yearbook, 1975, U.S. Bureau of Mines. Production of coal for 1974 is reported as 500 million metric tons/yr. Input figures represent total consumption multiplied by arsenic concentration (see Table IV).

3. Blackwood and Wachter (1978). National emission burden from coal storage piles is estimated at 630 metric tons/yr. Arsenic fugitve emissions data are calculated using previously reported concentrations of arsenic in coal.

4. EPA (1978). Screening sampling data for the coal mining industry. Acid mine drainage is reported to contain 12 mg/kg arsenic at an average flow of 1,004 mgd per mine. Drainage from 5,673 coal mines is considered in this calculation. Coal pile runoff is not considered in this estimate.

5. The amount of arsenic emitted to the atmosphere was calculated as follows:

the amount of arsenic in the fuel, A, was

$$A = (C)(F) \quad .$$

where C = concentration of arsenic in fuel, ppm

F = yearly consumption of fuel, metric tons/yr.

The amount emitted to the atmosphere, E, was

$$E = (A)(f)$$

where f = estimated fraction emitted to air.

$f_{coal} = 0.25$ (based on studies of 4 coal-fired units)

$f_{oil} = 1.0$

6. Minerals Yearbook, 1975. Based upon 77% of coal production used for electric power generation.

7. EPA (1976). Based upon 450 million metric tons/yr.

8. W. E. Davis and Associates, Inc. (1968). $f_{coal} = 0.27$.

9. EPA (1977); Screening sampling data for the steam electric power generating point source category; and EPA (1974); Development Document for the Steam Electric Power Generating Point Source Category. Arsenic is reported to be present in ash pond effluents at an average concentration of 448 mg/kg. The average flow from an ash pond is reported as 21.7×10^6 l/day-plant. 379 steam electric plants have been identified (NCA, 1977). Each facility is assumed to have an ash pond.

10. The breakdown of the boiler population used was: pulverized dry bottom 72.3%, pulverized wet bottons 13.5%, cyclone boilers 13.5%, and spreader stokers 0.7%. The particulate control efficiencies and the percentage of boilers using controls were multiplied and subtracted from unity to obtain the fractions of the total particulates that escape. For pulverized units this escape number is 0.11, for cyclone units 0.35, and for stokers 0.30.

11. The breakdown of the boiler population used was: pulverized dry 35% and stoker 65%. The particulate control efficiencies and the percentage of boilers using controls were multiplied and subtracted from unity to obtain the fractions of particulates that escape. For anthracite coal this escape number was estimated to be 0.40 based on age and control efficiency data.

12. The breakdown of the boiler population was: 38.9% tangential firing and 61.1% for all others.

13. The breakdown of the boiler population was: 38.9% tangential firing and 61.1% for all others. The particulate control escape number was 0.90. Total arsenic input was calculated to be 0.15 metric tons/yr.

14. Fuel consumption is taken from FPC (1972). Arsenic concentration data are taken from API (1973). Emissions are calculated by multiplying fuel consumption by arsenic concentration. Total arsenic input was calculated to be 0.059 metric tons/yr.

TABLE IV

ARSENIC EMISSIONS: Concentrations of Arsenic in Fuels and Waste Products

SOURCE	CONCENTRATION, mg/kg by weight		
	Fuel	Fly Ash	Bottom Ash
Coal			
Bituminous	28.0[1]	680 - 1,700[2]	0.448[3]
	14.02[4]		
	5.44[5]		
Anthracite	10.0[6]		
Petroleum			
Residual	0.30[7]	0	
Distillate	0.04[7]	0	
Synthetic Fuels			
Coal gas[8]			
Oil	82[9]		
Geothermal			

1. Magee, et al. (1973). Average values were calculated by each coal producing region.

2. Natusch, et al., 1974. Arsenic concentration is dependent upon flyash particle diameters: >11.3μ - 680 mg/kg; 7.3 - 11.3μ - 800 mg/kg; 4.7 - 7.3μ - 1,000 mg/kg; 3.3 - 4.7μ - 900 mg/kg; 2.1 - 3.3μ - 1,200 mg/kg; 1.1 - 2.1μ - 1,700 mg/kg.

3. EPA, 1978. Arsenic concentration in ash pond runoff. The arsenic concentration of slag is estimated to be on the order of 100 times less than that of flyash.

4. Ruch, et al., (1974). Mean analytical data for 101 coals, 81 of which are from the Illinois Basin. The remaining 10 coals are from the Eastern United States (11 samples) and Western United States (8 samples). Standard deviation for the mean value is 17.70 mg/kg; minimum value found 0.50 mg/kg; maximum value found 93.00 mg/kg.

5. W. E. Davis and Associates (1971). Data source unknown.

6. Kessler, et al. (1972). Analysis by SSMS.

7. API (1973).

8. Coal gas is not currently produced commercially. Preliminary studies indicate that 35% of the arsenic content of coal remains in the gasifier ash.

9. Hughes, et al. (1974). At this time, oil is not produced commercially from oil shale. No data are available concerning arsenic distribution between product oil and residue.

COPPER SMELTING

Arsenic, a significant contaminant of non-ferrous ores, is produced as a by-product of primary copper smelting at the ASARCo-Tacoma facility. Although Federal and State air pollution regulations have significantly reduced particulate emissions from copper smelters, they are still recognized as a major point source of atmospheric arsenic emissions.

Arsenic behavior during the pyrometallurgical processing of copper ore varies from smelter to smelter and is dependent on many factors including feed composition, temperature of the process material, blowing rates, gas composition and product purity. Thus, arsenic emissions may vary significantly not only for different smelter configurations, but also for smelters of similar configurations*.

All of the data that appears in Table V was obtained from a preliminary EPA draft of "Proposed National Emission Standard for Arsenic Emissions from Primary Copper Smelters" (EPA, 1979). This information was based on arsenic data received by EPA (in response to requests) from most of the domestic copper smelting facilities listed. When incomplete information was received, EPA made assumptions regarding the behavior of arsenic at a specific facility based on existing knowledge of the smelting configuration (or if need be, a similar configuration). Assumptions regarding the efficiencies of control devices (e.g., electrostatic precipitators) were frequently necessary to close the material balance. Although these material balances represent a substantial improvement in arsenic emissions data (heretofore, most calculations were based on outdated emissions factors), the precision of the data has not been verified.

---

* In general, the amount of arsenic present in the feedstock will affect the relative percentages of arsenic that are lost through volatilization and land-destined wastes.

TABLE V

ARSENIC EMISSIONS: Primary Copper Smelting, metric tons per year[1]

SOURCE	PRODUCTION		DISPERSION		
	Input[2]	Contained[3]	Air[4]	Land[5]	Water[6]
ASARCo					
Tacoma[7,8,9]	16,000	14,000	560	2,100	-
El Paso[9,10]	480	230	35	220	-
Hayden[11]	400	95[12]	200	120	-
Kennecott					
Hayden[13,14]	70	neg	35	40	-
Hurley[15,16]	neg	-	-	-	-
McGill[17,18]	70	neg	60	10	-
Garfield[19,20]	1,100	1,000[21]	10	85	-
Phelps Dodge					
Douglas[22,23]	85	neg	40	50	-
Morenci[22,24]	75	neg	30	50	-
Hidalgo[22,25]	160	5	5	150	-
Ajo[26]	550	30	310	220	-[27]
Magma[28]	35	neg	25	10	-
Copper Range/White Pine[29]	5	neg	3	3	-
Inspiration[30]	60	neg	5	55	-
Cities Service/Copperhill[31]	neg	-	-	-	-
Anaconda[32]	6,700	1,600	180	5,100	-
TOTAL	26,000	17,000	1,500[33]	8,200	

1. EPA, 1979 - except as noted. Data are reported to two significant figures and are rounded to five metric ton increments; emissions below three metric tons/yr are listed as negligible.
2. Input was calculated from arsenic feed data (lb/hr) and is based on smelter operation of 8,000 hr/yr. This operating factor was obtained from A. Vervaert, Office of Air Quality Programs and Standards, U.S. EPA, January 1979.

3. Includes arsenic contained in blister copper and dust recycled to lead plant. In the case of ASARCo /Tacoma, this figure also includes input to As_2O_3 reduction plant.
4. Air emissions (i.e., stack) include fugitive emissions under existing control conditions. Although these emissions were not included in the plant material balance, the error is assumed to be negligible.
5. This figure includes slag for dumping and sludge.
6. All acid plant waste is assumed to be land disposed (i.e., liquid effluent, such as acid plant purge water or scrubber sludge). Some scrubber blowdown waters are known to undergo lime treatment and settling with discharge to a central pond (Bhattacharyya et al., 1979).
7. Information on arsenic distribution at the Tacoma smelter was from Mr. K.W. Nelson, ASARCo Incorporated, by Mr. J. Padgett, EPA, March 1976.
8. Assumptions were made by EPA (1979) regarding the collection efficiency of the control equipment based on fugitive emission testing and operating temperatures.
9. Information on ASARCo /Tacoma, ASARCo /El Paso, and ASARCo /Hayden received from Mr. K.D. Loughridge, ASARCo Incorporated, by Mr. D.R. Goodwin, Director, EPA, ESED, October 9, 1975.
10. EPA distribution data is based on tests performed in April, 1977. Emissions data were calculated from basic assumptions of control equipment efficiencies and verified by telephone conversation by Mr. I. J. Weisenberg, Pacific Environmental Services with Mr. W. R. Kelly, Smelter Manager, ASARCo /El Paso on October 12, 1978. The fact that the El Paso smelting complex also processes lead and zinc was not reflected in the mass balances.
11. No smelter information is available on the distrubution of arsenic at ASARCo /Hayden. Assumptions were made based on similarities to the ASARCo /Tacoma and ASARCo /El Paso smelters.
12. Arsenic from the converter electrostatic precipitator is sent to El Paso.
13. Data for Kennecott/Hayden received in the correspondence from Mr. I. G. Pickering, Vice President Environmental Affairs, Kennecott Copper Corporation, to Mr. D. R. Goodwin, Director, ESED, U.S. EPA, May 9, 1978.

14. The arsenic material balance obtained from smelter personnel differs very slightly from that presented by EPA. To obtain a closed balance, several assumptions were made based on control equipment efficiency and tests performed.
15. Data for Kennecott/Hurley received in the correspondence from Mr. I. G. Pickering, Vice President Environmental Affairs, Kennecott Copper Corporation, to Mr. D. R. Goodwin, Director, ESED, U.S. EPA, May 9, 1978.
16. Arsenic feed and process contents obtained by the smelter personnel were based on triplicate analyses of monthly composites. Reverberatory stack emission samples were obtained from isokinetic tests performed. Stack emission results, however, are not necessarily representative of a long-term material balance. Arsenic imput reported as 1.41 metric tons/yr.
17. Data for Kennecott/McGill received in the correspondence from Mr. I. G. Pickering, Vice President Environmental Affairs, Kennecott Copper Corporation, to Mr. D. R. Goodwin, Director, ESED, U.S. EPA, May 9, 1978.
18. As the arsenic balance obtained from measured values at the smelter is incomplete, assumptions were made to complete the materials balance.
19. Data for Kennecott/Garfield received in the correspondence from Mr. I. G. Pickering, Vice President Environmental Affairs, Kennecott Copper Corporation, to Mr. D. R. Goodwin, Director, ESED, U.S. EPA, May 19, 1978.
20. Mass balance calculations are in agreement with the distribution presented by Mackey et.al., 1975 for the Noranda Process.
21. Dust from the electrostatic precipitators is stored for future sale.
22. Data for Phelps Dodge/Douglas, Phelps Dodge/Morenci, and Phelps Dodge/Hildago received in the correspondence from Mr. R. W. Pendleton, Jr., Vice President, Phelps Dodge Corporation to Mr. D. R. Goodwin, Director, ESED, U.S. EPA, June 2, 1978.

23. The arsenic mass balance was based on reported data, estimated collection efficiencies of the hot electrostatic precipitators, and assumptions made based on Stankovic, D. "Air Pollution Caused by Copper Metallurgy Assemblies in Bor" Institute for Copper, Bor, Project No. 02-513-1, U.S. EPA.

24. No arsenic distribution was available; therefore, assumptions were made on the basis of collection efficiencies for the control equipment, available information for the configuration of the fluidized bed-reverberatory-converter at Kennecott/Hayden and for the reverberatory furnace converter smelting configuration at the old Kennecott/Utah smelter.

25. Arsenic distribution information for the Hidalgo smelter was limited to spot checks at the facility. To successfully close the material balance, the distrubution presented by Koh(1972) for a similar process configuration (and "low" arsenic input) was considered.

26. All of the information used in calculating the mass balance were referenced to Schwitzgebel, 1978. Sampling by plant personnel and EPA occurred during 1976-1977. The results of arsenic sampling indicated that approximately 50 percent of the arsenic entering the smelter leaves in the reverberatory furnace off gas. Furthermore, as much as 90 percent of the arsenic entering the reverberatory furnace ESP may leave in the off-gas. Arsenic rates at the ESP outlet ranged from 25-140 lb/hr. (direct measurements). It should be noted that during a sampling period of a few days, the reverberatory furnace feed varies from 700 mg/kg to 7,000 mg/kg.

27. Acid plant purge water is reported as 27 lb/hr arsenic, in EPA (1978) as opposed to the value of 14.2 lb/hr reported as acid plant waste in the EPA (1979) mass balance for the Ajo plant.

28. Information on the input and materials balance was obtained from D.R. Ridinger, Director of Environmental Affairs, Magma Copper Company to Mr. D. R. Goodwin, Director, ESED, U.S. EPA, dated April 4, 1978. No information was given by the manufacturer on sampling procedures. To close the material balance, EPA made assumptions concerning arsenic reporting in the blister, volatization in the converters, and ESP efficiency.

29. Information concerning the arsenic feed and distribution was obtained from correspondence from J. W. Maksyn Environmental Control Engineer, White Pine Copper Division, Copper Range Company to D. R. Goodwin, Director, ESED, U.S. EPA, dated September 7, 1978. To obtain the arsenic mass balance, assumptions were made from data on similar process configurations.

30. Arsenic data was obtained from correspondence from Mr. M. W. Anderson, Inspiration Consolidated Copper Company to Mr. D. R. Goodwin, Director, ESED, U.S. EPA, dated November 20, 1978. Information from the literature was used to supplement incomplete smelter data in performing an arsenic distribution and mass balance.

31. Information on the arsenic content of the copper concentrate was received from S. L. Norwood, Manager, Environmental Control, Cities Service Company to Mr. D. R. Goodwin, Director, ESED, U.S. EPA, dated September 5, 1978. As arsenic input is estimated at 0.36 metric tons /yr, the emissions were considered negligible, and any attempt at a distribution to be of questionable accuracy.

32. Anaconda test data provided smelter feed concentrates. The mass balance presented is the result of (1) tests on process samples obtained from Anaconda; (2) a rough mass balance calculated by the EPA contractor; and (3) a refined mass balance provided by Anaconda (See: Correspondence from Mr. R. L. Sloan, The Anaconda Company, to Mr. I. J. Weisenberg, Pacific Environmental Services, October 11, 1978).

33. Process gases from all three major smelting operations are combined into a main flue duct and transported to a filtration plant for particulate removal prior to being discharged to the atmosphere through the main stack.

COPPER REFINING

The blister copper, derived from copper concentrates, may be fire-refined to "anode" copper with a specification of 75 mg/kg maximum arsenic content. Electrolytic refining is reported to reduce the arsenic content to approximately 5 mg/kg.

The data presented in Table VI are largely based on average arsenic concentrations of copper during the various stages of refining, as reported by EPA (1976a). An inconsistency in the value cited for the average arsenic content of the input anode copper (1,000 mg/kg) could not be reconciled with the reported specification for fire-refined casting copper (i.e., anode copper). However, as the arsenic content of sampled blister and anode coppers were approximately the same, the arsenic loss during the casting process was assumed to be negligible (EPA, 1976a). The arsenic removed from the anode copper is found in the slime from the electrolysis cells and in the electrolyte. The resulting arsenic-bearing wastes are disposed of on land as a slag/sludge.

Conflicting estimates of arsenic emissions attributable to refined copper production are presented by NAS(1977), as derived from Davis and Associates (1971). These figures appear to be useless, as they combine smelting and refining operations, neglecting to point out that nearly all of the arsenic emissions from refining are land-destined (See Table VI). Furthermore, using this emission factor (apparently based on 1968 data) and 1974 production figures gives a combined result which is substantially lower than that for copper smelters alone in 1974.

Lake copper, or native copper, is not derived from concentrates. Arsenic content varies from 25 mg/kg to 5,000 mg/kg. An average value of 500 mg/kg was used by EPA(1976a) to calculate the total quantity of arsenic contained in this copper.

TABLE VI

ARSENIC EMISSIONS: Copper Refining, metric tons per year[1]

SOURCE	PRODUCTION		DISPERSION		
	Input[2]	Contained	Air	Land	Water
Electrolytic	1,400[3]	7[4]	-[5]	1,400[6]	40[7] 400[8]
Casting	630[9]	7[10]	-	-[11]	
Lake	30[12]		-		

1. All data are reported to two significant figures and rounded to 5kkg increments.
2. Minerals Yearbook, 1975. All data for primary refined copper (domestic and foreign ores) are for 1974.
3. EPA, 1976a. Based on an average arsenic content in the input anode copper of 1,000 mg/kg. Electrolytic copper refined in 1974 totaled 1,400,000 metric tons.
4. EPA, 1976a. Electrolytically-refined copper contains arsenic at levels reported as 1 to 10 mg/kg and 4 to 11 mg/kg. Assuming an average arsenic concentration of 5 mg/kg, the quantity of arsenic in the product copper is estimated to be 7 kkg/yr.
5. NAS, 1977. An arsenic emission factor of 0.000955kg/kkg of copper produced (smelting and refining) was presented based on Davis (1971) and the Minerals Yearbook, 1968. However, an average arsenic emission of 0.00105kg/kkg was reported for copper smelters in 1974. These emission factors cannot readily be reconciled, as electrolytic refining results in land-destined emissions rather than in atmospheric emissions.
6. EPA, 1976a. Arsenic residues are reported to be land-disposed as slag.
7. EPA, 1976a. Effluents from electrolytic refining were reported as 0.03kg arsenic/kkg copper product (See: EPA, 1975).
8. EPA, 1978. An estimated total annual discharge from copper manufacturing based on an unsubstantiated emission factor and 1976 arsenic trioxide production.
9. EPA, 1976a. Based on average arsenic content in the input blister copper of 88 mg/kg. Casting copper production totaled 79,000 metric tons in 1974.

10. EPA, 1976a. Based on a specification of 75 mg/kg maximum arsenic content of fire-refined casting copper. The discrepancy between this specification and the average arsenic content of anode (i.e., fire-refined copper) copper reported in Footnote 3 could not be reconciled.

11. EPA, 1976a. Discrepancies between the arsenic specifications for fire-refined copper and the reported arsenic concentrations of anode copper, make calculation of land-destined wastes meaningless.

12. EPA, 1976a. Lake or elemental copper is not derived from concentrates. Furthermore, there are three grades of lake copper: prime, which contains 25 mg/kg arsenic; natural, which contains 200 to 600 mg/kg arsenic; and arsenical, which contains 600 to 5,000 mg/kg arsenic. Thus, an average value of 500 mg/kg was used to calculate the total quantity of arsenic in lake copper (based on production of 60,000 metric tons in 1974).

PRIMARY LEAD AND ZINC PRODUCTION

The production of primary zinc and lead, requiring smelting and pyrometallurgic or electrolytic refining methods, are additional sources of arsenic emissions to the environment. The estimates of input arsenic, as shown in Table VII, unfortunately are based on averages of foreign ore concentrates. Atmospheric emission factors calculated by Davis (1971) or Anderson (1973) have not been substantiated; furthermore, such factors do not apply to electrolytic slab zinc production. Changes in zinc smelting and refining facilities, as indicated by the Minerals Yearbook, 1975, are not reflected by these figures.

NAS states no new data on emission from zinc and lead smelters were available for inclusion in their report (NAS, 1977). However, on the basis of indicated smelter inputs of arsenical and nonarsenical concentrates (including some supplementary information obtained on the arsenic content of ores and concentrates) and estimate stack losses, NAS derived recovery factors similar to those arrived at earlier by Davis (1971).

TABLE VII

ARSENIC EMISSIONS: Primary Lead and Zinc Industries, metric tons per year[1]

SOURCE	PRODUCTION			DISPERSION		
	Input	Contained	Emission Factor[2]	Air	Land	Water
Lead[2]	1,100	20[4]	0.0004[5]	240[6]	800	-
Zinc			0.0006[7]	300[8] 70[9]		
	310[10] 210[10]	215[13]	0.00065[5,11]	190	120	neg[12]

1. Data are reported to two significant figures and are rounded to 5kkg increments; emissions below 3kkg are considered to be negligible.
2. Suta, 1978. Fugitive emissions are estimated to be 10 percent of stack emissions.
3. EPA, 1976a. An average Pb/As concentration ratio of 1,400 mg/kg (based on foreign ore concentrates) was used to estimate the overall quantities of arsenic contained in lead concentrates. Based on this concentration and lead production of 610,000 kkg/yr the quantity of arsenic is calculated to be 850 metric tons/yr. An additional 210 metric tons/yr enters the primary lead industry via residues from the electrolytic zinc industry. Using the emission factor of Davis (1971), the arsenic lost to the atmosphere was computed to be 240kkg. No appreciable quantities of arsenic were found in the wastewaters from the primary smelters. Thus, the remaining 610kkg of arsenic, plus 210kkg/yr in residues from the zinc industry, were distributed between land-destined wastes and that portion retained in the refined lead (EPA, 1976a).
4. EPA, 1976a. Based on an annual primary lead production of 610,000 metric tons in 1974 containing 35 mg/kg arsenic (an average of ASTM standard B29-55 which specifies an arsenic content of 20 mg/kg for undesilverized lead and 50 mg/kg for desilverized lead), refined lead contains approximately 20 metric tons of arsenic.
5. Emission factor calculated by Davis (1971) based on 1968 estimates. This factor was obtained through personal contact with processing companies, and on engineering calculations supported by data concerning smelter flow rates and temperature.
6. EPA, 1976b. Estimated arsenic emissions for primary lead production in the U.S. for 1974. This figure was calculated using EPA emissions factors (0.0004kg/kkg of lead produced) and by applying "appropriate levels of control". (See: Anderson, 1973).

7. NAS, 1977. Arsenic emissions factor for zinc smelting and refining based on Davis (1971) and Minerals Yearbook, 1968.

8. Minerals Yearbook, 1975. Based on 1974 primary slab zinc production of 504,000 metric tons.

9. EPA, 1976b. Estimated arsenic emssions for primary zinc production in the U.S. for 1974. This figure was calculated using EPA emissions factors (0.5 kg/kkg of zinc produced) and by applying "appropriate levels of control". (See: Anderson, 1973.)

10. EPA, 1976a. An average As/Zn concentration ratio of 1,050 mg/kg (based on foreign ore concentrates) was used to estimate the total quantity of arsenic in primary zinc. Based on a 1973-1974 production level of 490,000 kkg/yr of slab zinc, an estimated 290,000 kkg/yr are produced from pyrometallurgical zinc smelters and an estimated 200,000 kkg/yr at an electrolytic facility.

11. EPA, 1976a. This emission factor applies only to pyrometallurgical zinc smelters.

12. EPA, 1978. An estimated 1.3 metric tons are discharged annually from zinc smelting and refining.

13. EPA, 1976a. Residues shipped to lead smelters contain almost all of the 210 metric tons/yr of arsenic originally present in the zinc concentrates electrolytically refined. Based on maximum levels of arsenic in refined zinc of all commercial grades, an estimated 5 metric tons/yr is contained in zinc products.

PRIMARY NON-FERROUS ORES, MINING AND MILLING

The mining and milling of primary non-ferrous metal ores are another source of arsenic emissions for which little hard data are available. Production figures are from the Minerals Yearbook, 1975, and pertain to ore production except as footnoted (this may account for any inconsistencies with figures presented by EPA(1976a)). Emission factors reported by NAS are based on 1968 data and cannot be verified (NAS, 1977). NAS further states that an estimated 40 percent of the arsenic in copper or copper-lead-zinc ore is left in the concentrator tailings, which are deposited on land and subject to wind losses. Similarly, arsenic in gold and uranium mill tailings are subject to wind losses. Reported water discharges are based on EPA Effluent Guidelines Division screening and sampling data (EPA, 1978).

As data are scarce on smelting and refining operations for most non-ferrous metals (with the exception of copper, zinc, and lead), a separate table has not been included. EPA made a very rough approximation of the quantities and fates of arsenic in these non-ferrous metal ores; however, their analysis (See Footnote 2, Table VIII) has not been verified (EPA, 1976a).

TABLE VIII

ARSENIC EMISSIONS: Primary Non-Ferrous Metal Ores Mining and Milling, metric tons per year[1,2]

SOURCE	Production[3]	Emission Factor x 10^6[4]	DISPERSION		
			Air	Land	Water
Copper	270,000,000	.45	120		400[5]
Lead	600,000	.45	neg		
Zinc	450,000	.45	neg		540[6]
Aluminum (Bauxite)	1,900,000				290[7]
Antimony	600				
Gold	240,000[8]	.45	neg		
Manganese	270,000				
Mercury	75				
Silver	1,100	.45	neg		
Tin	- [9]				
Uranium	6,500,000[10]	.45	neg		
Vanadium	4,800[11]				

1. All data reported to two significant figures and rounded to 5kkg increments. Emissions less than 3kkg/yr are considered negligible.
2. EPA, 1976a. With the notable exceptions of copper, lead, and zinc, little data are available on the arsenic content of primary non-ferrous ores. Further, data are scarce on arsenic emissions which occur during mining, milling, smelting, and refining operations. Based in part on antimony data (e.g., arsenic occurs at a concentration of roughly 3 percent in antimony ores) and in part upon similarities to the lead-zinc industry, EPA (1976a) assumed that: arsenic is 1 percent of the quantity of gold, silver, mercury, uranium, vanadium, and antimony concentrates; furthermore, one-third is recovered as sulfides, that one-third is lost to air emissions, and that one-third is in land disposed wastes.

3. Minerals Yearbook, 1975. All mine production data for 1974, except as noted.

4. NAS, 1977. Based on Davis (1971) and Minerals Yearbook, 1968; reported in terms of metric tons/metric tons of ore produced.

5. EPA, 1978. Based on Effluent Guidelines Division screening sampling data for copper mine effluents and average discharge rates for 9 direct discharges.

6. EPA, 1978. Based on Effluent Guidelines Division screening sampling data for lead/zinc mines and average discharge rates for 34 direct discharges.

7. EPA, 1978. Based on estimated annual discharges from two plants engaged in the processing of bauxite ore to produce alumina (with average discharges of .26 metric tons/day for 300 days).

8. Minerals Yearbook, 1975. Represents gold ore and old tailing to mills in 1975.

9. Minerals Yearbook, 1975. Information withheld for proprietary reasons.

10. Minerals Yearbook, 1975. Represents mine production of ore (not U_3O_8 content) and does not include output of approximately 200 tons of U_3O_8 from mine waters, leaching operations, and recovery from phophate rock processing. The U_3O_8 content of the ore after milling was 11,000 metric tons.

11. Minerals Yearbook, 1975. Mine production of vanadium in the U.S., as measured by receipts of uranium and vanadium ores and concentrates at mills (vanadium content).

MANGANESE PRODUCTION

Manganese ferroalloys are produced from manganese ore by smelting in blast or electric furnaces. Since arsenic data for manganese smelting are scarce, EPA(1976a) has estimated these emissions by making an analogy "to the transport of the chemically-similar phosphorus: 60 percent of the phosphorus in the ore passes into the ferroalloy, 30 percent passes into the slag and 10 percent escapes with furnace gases." (See Table IX).

About 10 percent of the manganese ore is used for making carbon-zinc and alkaline manganese dioxide dry cell primary batteries, and for use in the chemicals and glass industries. The estimated 400 metric tons per year of arsenic dissipated in such end products was based on an average manganese ore content of 0.20 percent. This value was derived from analyses of three foreign manganese ores (i.e., Brazilian and Mexican)* with arsenic concentrations ranging from 0.15 to 0.25 percent (EPA, 1976a).

---

*EPA, 1976a. Manganese ore consumed in the U.S. with 35 percent or more manganese content is imported principally from Africa and Brazil.

TABLE IX

ARSENIC EMISSIONS: Manganese Production, metric tons per year[1]

SOURCE	PRODUCTION		DISPERSION		
	Input	Contained	Air	Land	Water
Smelting	4,000[2]	3,200[3]	10[4]	350[5]	
Non-ferrous manganese ore consumption		400[6]			

1. All data are reported to two significant figures and rounded to 5kkg increments.
2. EPA, 1976a. Based on an average domestic industrial consumption of manganese ores of 2.0 million metric tons per year and an average value of 0.20 percent arsenic.
3. EPA, 1976a. Little data are available as to the fate of arsenic during the smelting process. Using the analogy of phosphorus in ferroalloy production, an estimated 2,200 metric tons per year are retained in ferroalloys (consumed in iron and steel) and 1,100 metric tons per year contained in slag from ferroalloy furnaces. (As a result of independent rounding, the total is higher than the contained figure listed.)
4. EPA, 1976a. Estimated air emissions from furnaces.
5. EPA, 1976a. Estimated dusts collected from furnaces.
6. EPA, 1976a. Estimated arsenic content of non-ferroalloy manganese ore dissipated in end-products.

IRON AND STEEL PRODUCTION

Arsenic emissions from iron ore production and steelmaking are presented in Table X, compiled largely from data presented by EPA (EPA, 1976a). According to NAS, only insignificant quantities of arsenic are emitted during iron and steel production (NAS, 1977).

The average arsenic concentration in iron ore requires further analysis; EPA (1976a) assumed it to be 400 mg/kg for purposes of their study. NAS (1977) reports a range of 1 to 2,900 mg/kg of arsenic in sedimentary iron ores, with an average value of 400 mg/kg. Therefore, all figures based on an input arsenic concentration of 400 mg/kg should only by considered as a rough approximation (i.e., order of magnitude indicator).

As is discussed in the footnotes of Table X, EPA's estimates are based on 5-year averages of iron ore consumption and pig iron production. Several assumptions are made as to the arsenic losses during steelmaking, based on analogies to phosphorus, for both basic oxygen and basic open hearth processes. A 99 percent dust collection efficiency was assumed to obtain the air emission; the collected dust is presumed to be disposed of as landfill. The largest portion of arsenic input is contained in the slag and resulting steel products.

TABLE X

ARSENIC EMISSIONS: Iron Ore Production and Steelmaking, metric tons per year[1]

SOURCE	PRODUCTION		DISPERSION		
	Input	Contained	Air	Land	Water
Crude Ore[2]	88,000[3]		9[4]		
Iron Ore/Pig Iron	54,000[5]	54,000[6]			
Cast Iron	-[7]	3,300[8]	20[9]	100[9]	
Steelmaking	51,000[10]	49,500[11]	12[12]	1,200[13]	

1. All data are reported to two significant figures and rounded to 5kkg increments.
2. Minerals Yearbook, 1975. In 1974, 220,000,000 metric tons of crude iron ore were mined in the U.S.
3. EPA, 1976a. An arsenic concentration of 400 mg/kg is reported in iron ore but is unsubstantiated. No data was reported on arsenic emissions attributable to iron ore mining.
4. Anderson, 1973. An unsubstantiated mining emission factor of 0.1kg/kkg of arsenic present in the ore is reported.
5. EPA, 1976a. Based upon an assumed arsenic concentration of 400 mg/kg (from U.S.G.S. and U.N. references), and an average iron ore consumption from 1970 to 1974 of 134.5 million metric tons per year.
6. EPA, 1976a. The arsenic is assumed to be retained in the pig iron.
7. EPA, 1976a. A cast iron production level of 17.2 million metric tons per year is reported; the 2.4 million metric tons per year of pig iron, which is used for cast iron production via cupola and similar furnaces, is augmented by 14.8 million metric tons per year of scrap. No arsenic content of the scrap was reported.
8. EPA, 1976a. A reported average of 5 million metric tons per year of pig iron were consumed during 1970-1974 for cast iron products. Thus, with an arsenic concentration of 650 ppm, 3,300 metric tons are retained in cast iron.
9. EPA, 1976a. Based on an average uncontrolled emission factor for arsenic from cast iron production of 0.007kg/kkg of metal charged (See: Anderson, 1973). An estimated 20 metric tons per year are released to the atmosphere, with the remaining 100 metric tons collected and disposed of on land.

10. EPA, 1976a. Based on an average 78 million metric tons per year of pig iron consumed in steelmaking with an average arsenic content of 650 ppm.

11. EPA, 1976a. Includes an estimated 14,900 metric tons per year of arsenic contained in steel and an estimated 34,600 metric tons per year in slag from steelmaking furnaces. The latter estimate was not substantiated; furthermore, as the slag is widely used, (e.g., railroad ballast, highway base or shoulders, etc.) it was categorized as contained arsenic.

12. EPA, 1976a. Assumes a 99 percent dust collection efficiency and that the arsenic in the uncontrolled dust emissions is the same concentration level as it is in the steelmaking charge.

13. EPA, 1976a. Collected steelmaking dusts are assumed to be land disposed.

PHOSPHORUS PRODUCTION

Arsenic is a common trace constituent of phosphate rock and, for Florida rock at least, is a linear function of iron oxide present in the rock (Stow, 1969). Arsenic content of Western rock, has been suggested to be dependent upon the organic carbon content of the rock (Gulbrandsen, 1966). Arsenic input is based on quantities of marketable phosphate rock consumed in 1972, phosphorus concentration for each type of rock, and As/P_2O_5 ratios for each type of rock (See Footnote 2 of Table XI).

The arsenic present in phosphate rock is suggested to follow phosphorus quantitatively, whether the acidulation (conversion to phosphoric acid) or the furnace process (reduction to elemental phosphorus) is used. Phosphorus is not recovered quantitatively from phosphate rock; phosphorus (and arsenic) not recovered is assumed to be land-disposed in sludge ponds. In Table XI non-agricultural production represents phosphorus produced by the furnace process. Arsenic is removed from food grade phosphoric acid, generally by sulfide precipitation; arsenic is also removed in the manufacturing processes of phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride. EPA has estimated that all arsenic associated with miscellaneous uses is land-disposed (EPA, 1976a). Arsenic present as an impurity in phosphate detergents is assumed to be discharged to surface waters. All other arsenic is assumed to be dissipated with the end product.

TABLE XI

ARSENIC EMISSIONS: Phosphorus Production, metric tons per year[1]

SOURCE	PRODUCTION		DISPERSION		
	Input[2]	Contained[3]	Air	Land[3]	Water
Production (Total)	770				
Florida Rock	450	170		65	
Domestic fertilizer	240				
Animal feed	15				
Exports	190	190			
Tennessee Rock	40	30		10	
Non-agricultural	40				
Western Rock	270	200		60	
Domestic fertilizer	50				
Animal feed	15				
Non-agricultural	190				
Exports	15	15			
Use					
Domestic fertilizer	290		neg[4]	290	
Animal feed	30			30	
Detergents[5]	110	110			110
Phophoric acid (food grade)	60			60	
Miscellaneous	60			60	
Export	200	200			

1. EPA, 1976a. Based on 1972 marketable phosphate rock consumption for 1972. Data are reported to two significant figures and are rounded to the nearest 5kkg increment; emissions below 3kkg are considered to be negligible.

2. Arsenic input is calculated on the basis of the following As/P_2O_5 ratios: Florida rock - 0.000045; Tennessee rock - 0.000082; Western rock - 0.000230.

3. EPA, 1976a. Arsenic in phosphate rock is suggested to follow phosphate recovery quantitatively (EPA, 1976a). Arsenic dispersion is thus calculated on the basis of phosphate recovery from marketable rock: Florida rock - 66%; Tennessee rock - 73%; Western rock - 77%. Arsenic not recovered is assumed to be land-disposed in sludge ponds.

4. Anderson, 1973.

5. EPA, 1976a. Arsenic in household detergents and presoaks was measured at concentrations ranging from 2 to 59 ppm (Angino, et al. 1970). The production of trisodium phosphate has been reported to have been reduced because of the environmental concern over phosphorus in wastewaters.

BORON PRODUCTION

Approximately 80 percent of the U.S. production of borax is from ore deposits, the remainder is obtained from saline brines. The arsenic content varies widely within a given ore horizon (e.g., from 0 to 1,000 mg/kg); however, EPA indicates that the residue from the digested ore contains approximately 45 mg/kg of arsenic (EPA, 1976a). Saline brines pumped from beneath the crystallized surface of Searles Lake in Southern California contain 500 mg/kg sodium arsenate, or the equivalent of 180 mg/kg arsenic. As the brines are processed and returned directly to the lake (plus added process waters), almost all of the arsenic initially extracted from the lake (with the exception of that contained in the borax product) is assumed returned to the lake bed.

Table XII presents arsenic emissions for boron production based on EPA calculations (EPA, 1976a). A value for land-destined arsenic wastes resulting from borax ore production was derived from the estimated arsenic content of the ore residue and the total amount of residue produced. The concentration of arsenic contained in the borax ore was arrived at by calculations. It was assumed that the arsenic found in wastewaters from boric acid production represents all of the arsenic originally present in the technical grade borax. No wastewater sampling data were presented.

TABLE XII

ARSENIC EMISSIONS: Boron Production, metric tons per year[1]

SOURCE	PRODUCTION		DISPERSION		
	Input	Contained	Air	Land	Water
Production[2]					
Borax Ore	50[3]	20[4]		30[5]	
Borax from Brines	2,200	5[4]		2,200[6]	
Borax Use					
Boric acid[7]	5				5
Other borax products[8]	20	20			

1. EPA, 1976a. Data are reported to two significant figures and are rounded to the nearest 5kkg increment; emissions below 3kkg are considered to be negligible. U.S. production of boron minerals has averaged 1,070,000 metric tons per year from 1972 to 1974 which corresponds to an annual boron oxide production of 580,000.

2. Commodity Data Summaries 1975; Minerals Yearbook 1972. Approximately 80% of U.S. production is from ores and 20% from brines.

3. EPA, 1976a. Arsenic occurs in widely varying concentration in a given ore horizon. This figure represents the sum of contained and dispersed arsenic.

4. EPA, 1976a. This figure is derived by assuming that the arsenic in boric acid wastewaters represents the entire amount of arsenic in borax raw material. Thus, technical grade borax is estimated to contain approximately 21 mg/kg of arsenic.

5. EPA, 1976a. Residue from digested ore is approximately 0.8 metric tons per metric ton of borax product. This residue contains approximately 45 mg/kg of arsenic. This residue is placed in ponds.

6. EPA, 1976a. Sodium borate is extracted from Searles Lake brine which contains 500 mg/kg sodium arsenate (equivalent to 180 mg/kg arsenic). Total brine processed is approximately 12×10^9 liters per year. Depleted brines plus process wastewaters are returned to the lake.

7. EPA, 1976a. 110,000 metric tons of boric acid are produced annually. 36 grams of arsenic are discharged in process wastewaters per metric ton of boric acid produced.

8. EPA, 1976a. Consumption of other borax products is approximately 880,000 metric tons per year. Arsenic concentration in this borax is assumed to be 21 mg/kg.

WATER AND WASTEWATER

Arsenic input and emissions from individual water/wastewater facilities depend on the individual raw wastewater loadings and resultant removal efficiencies. Variation of input is largely dependent on industrial discharges in the case of POTW's, and on the raw water source of a water treatment plant. As shown in Table XIII, arsenic emissions from POTW's are approximated from (1) estimates of dry sludge generation and the average arsenic content of the sludge and ; (2) estimates of the effluent quality and total combined daily flow. In the case of water treatment plants, arsenic emissions are described in terms of per capita water consumption and treatment efficiencies. Thus, all of the numbers presented can only be considered as rough approximations of the actual arsenic emissions.

TABLE XIII

ARSENIC EMISSIONS: Water and Wastewater Treatment, metric tons per year[1]

SOURCE	Input	DISPERSION		
		Air	Land	Water
POTW[2,3], Municipal Water Treatment		neg[4,5]	neg[4,5] 65[7]	160[6]

1. All data are reported to two significant figures and rounded to 5 kkg increments. Emissions below 3 kkg/yr are considered negligible.
2. Publically owned treatment works.
3. EPA, 1976a. At one secondary treatment plant, the arsenic in thickened waste sludge was reported as 61 μg/kg; at an assumed 8 percent solids content, the sludge solids would have contained 0.75 mg/kg arsenic. Assuming that per capita sludge generation is 0.09 kg/day and 120 million people are served by POTW's, (generating 4 million kkg/yr of dry sludge) 3 metric tons of arsenic are contained in sludge.
4. EPA, 1976a. An arsenic emission factor or 0.01 kg/kkg of "sewage and sludge" is reported by EPA (Anderson, 1973). By assuming a solids concentration of 20 percent in dewatered sludge (feed to an incinerator), the emission factor is then equivalent to an arsenic concentration in dry sludge of 2 mg/kg, implying that all the arsenic is volatized. According to EPA (1976a), one-third of all sludge is incinerated, thus, one metric ton of arsenic is emitted to the air, while 2 kkg are applied to land.
5. Furr, et al. 1976. Based on an average of reported arsenic concentrations found in municipal sludges from 16 American cities, arsenic concentration is 14 mg/kg on a dry weight basis. Assuming 4 million metric tons of dry sludge are generated per year, 56 metric tons of arsenic are contained in sewage sludge. What portion of this sludge is land-disposed or incinerated is unknown.
6. EPA, 1978. Based on calculated averages of arsenic concentrations from selected facilities and a total combined daily flow from POTW's of 23,000 mgd.
7. EPA, 1976a. Based on an estimated removal rate of 2.7 μg/liter per year and an estimated per capita water use of 200,000 liters per year (or 24×10^{12} liters per year for 120 million people).

SECTION III

SUMMARY AND CONCLUSIONS

The purpose of this study was to compile existing information on arsenic emissions to the environment from natural and anthropogenic sources in the form of preliminary materials balances. Although verification of existing data was outside the scope of work, a major goal of this report was to establish a range of uncertainty for the figures cited. This objective was achieved by presenting the arsenic emissions data in a fully annotated tabular format.

Prior to this study, considerable effort had been expended by the EPA and NAS to assess the environmental and health effects of arsenic and its compounds. While their studies required evaluation of emission sources, much of the arsenic data represents a "rehashing" of old numbers (i.e., many numbers were originally educated guesses or unsubstantiated engineering judgments. Furthermore, certain emissions figures, as noted within the text of the report, appear of little use because (1) primary sources neglected to indicate error ranges; and (2) emissions factors were not properly utilized (e.g., emissions factor applied to incorrect production or arsenic input data).

What the existing arsenic data has provided, however, is a framework for constructing gross estimates of arsenic distribution in the environment. From the results of this preliminary analysis, three major sources of environmental emissions emerge: energy production, arsenic production and use, and primary copper smelting. Other nonferrous smelters, specifically primary lead and zinc smelters, may represent another significant source of arsenic to the environment. In terms of human exposure, other sources appear to be of much less consequence.

The most complete information on arsenic release to the environment was found for primary copper production; the data is contained in a recently developed preliminary draft of arsenic discharges from individual copper smelters (EPA, 1979). This, unfortunately, is not the case for other point

source categories.

Multimedia arsenic materials balances for primary lead and zinc smelting were not available at the time this report was prepared. Most data points cited were based on emission factors that may not adequately reflect current control technologies. No discussion of secondary nonferrous smelters was included in this report, as arsenic data is limited. According to Suta (1978), estimated arsenic emissions from secondary smelting operations results in insignificant atmospheric concentrations.

Arsenic emissions from the energy sector are dependent on fuel consumption and feed concentrations. While fuel consumption is relatively well-qualified, simple averages are inadequate to describe arsenic concentrations in 4,000 coals.

Finally, most reported figures for arsenic emissions during arsenic production and use (i.e., in the manufacture of commercial products or from arsenic added to commercial products) are speculative. This is a direct result of the proprietary nature of such data.

Recommendations for further data collection and evaluation include:

- Examine existing arsenic concentration data for U.S. coals. This information can be located in the files of the U.S. Geological Survey (Coal Resources Branch) and Penn. State Data Base. Pursue other avenues of data generation, such as on-going studies sponsored by other government agencies (e.g., Department of Energy) or the National Coal Association. Map arsenic emissions (to all three media) for coal-fired electric utilities on the basis of capacity, existing control technologies, and representative arsenic feed concentrations.

- Extend existing data sources to include EPA proprietary files and, if possible, Stanford Research Institute manufacturing/marketing projections for arsenical pesticide production.

- Obtain arsenic data collected for primary non-ferrous smelters and held by NIOSH (See: "Control Technology Summary Report on the Primary Non-Ferrous Smelting Industry", Radian Corporation, December 1978).

- Verify existing emission factors for non-ferrous smelters. Evaluate emissions from secondary smelters, specifically those processing anitmonial lead.

- Review existing literature for arsenic concentration data that could be of use in evaluating unsubstantiated emission factors (See: Suta, 1978; Union Carbide Corp., 1976; and Holt and Moberly, 1976).

- Address arsenic emissions from non-point sources, such as mining and agricultural runoff. Compare findings with existing leachate data to determine potential hazard.

After completing these tasks, the need for a sampling and analysis program must be weighed against the population at risk.

REFERENCES

Anderson, David, "Emission Factors for Trace Substances", U.S. Environmental Protection Agency, EPA-450/273001, December 1973.

Angino, E. E., L. M. Magnuson, T. C. Waugh, O. K. Galle, and J. Bredfeldt, "Arsenic in Detergents: Possible Danger and Pollution Hazard", Science 168: 388-90, April 17, 1970; Discussion 170: 870-2, November 20, 1970.

API, "Validation of Neutron Activation Technique for Trace Element Determination in Petroleum Products", American Petroleum Institute, API Report 4188, Washington, D.C., 1973.

Attari, A., "Fate of Trace Constituents of Coal During Gasification", EPA-650/2-73-004, U.S. Environmental Protection Agency, 1973.

Bhattacharyya, D., A. B. Jumawan, Jr., R. B. Grieves, "Charged Membrane Ultrafiltration of Heavy Metals from Non-ferrous Metal", Journal of Water Pollution Control Federation 51, 76, 1979.

Blackwood, T. R. and R. A. Wachter, "Source Assessment: Coal Storage Piles", U.S. Environmental Protection Agency, EPA-600/2-78-004k, May 1978.

Boyle, R. W. and I. R. Jonasson, "The Geochemistry of Arsenic and its Use as and Indicator Element in Geochemical Prospecting", J. Geochem, Explor., 2, 251, 1973.

Bureau of Mines, 1975 Minerals Yearbook Vol I: Metals, Minerals, Fuels, U.S. Department of Interior, Bureau of Mines, 1977.

Commodity Data Summaries, 1975, Bureau of Mines, 1977.

Conway, E. J., Mean Geochemical Data in Relation to Oceanic Evaluation", Proc. R. Irish Acad. 48, 152, 1942.

Chu, T. J., R. J. Ruane, and G. R. Steiner, "Characteristics of Wastewater Discharges from Coal-Fired Power Plants", Proceedings of the 31st Industrial Waste Conference, Purdue University, 1976.

Cox, D. B., J. Chu and R. J. Ruane, "Quality and Treatment of Coal Pile Runoff", NCA/BCR Coal Conference, 1977.

Davis, W. E. and Associates, National Inventory of Sources and Emissions: Arsenic - 1968, PB 220 619, May 1971.

Durum, W. H., "Occurrence of Some Trace Metals in Surface Waters and Groundwaters", Proceeding Sixteenth Water Quality Conference, University of Illinois, February 12-13, 1974.

EPA, 1974, "Development Document for Effluent Limitations Guidelines Documents and New Source Performance Standards for the Steam Electric Power Generating Point Source Category", EPA 440/1-74/029-a, U.S. Environmental Protection Agency, 1974.

EPA, 1976a, "Technical and Microeconomic Analysis of Arsenic and Its Compounds", U.S. Environmental Proetection Agency, EPA 560/6-76-016, April 1976.

EPA, 1976B, "Air Pollutant Assessment Report on Arsenic",U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, 1976.

EPA, 1976c, "Development Document for Interim Final Effluent Limitations Guidelines for the Pesticide Chemicals Manufacturing Point Source Category", U.S. Environmental Protection Agency, EPA/440/1-75/060d, November 1976.

EPA, 1977, Screening sampling data for the steam electric power generating point source category, U.S. Environmental Protection Abency, Effluent Guidelines Division, 1977.

EPA, 1978, "Gross Annual Discharge to the Waters in 1976: Arsenic", Revised Report No. 2, U.S. Environmental Protection Agency, April 1978.

EPA, 1979, "Preliminary Draft: Environmental Assessment of Arsenic Emissions from Copper Smelters", U.S. Environmental Protection Agency, OAQPS, Research Triangle Park, (DRAFT), January 1979.

Ernst and Ernst, "Wood Preservation Statistics", Proceedings of the American Wood Preservers Association, 72 265, 1976.

FPC, "Gas Turbine Electric Plant Construction Cost and Annual Production Expenses", Federal Power Commission, 1972.

FPC News, Federal Power Commission, 1974.

Ferguson, I. F. and J. Gavis, "A Review of the Arsenic Cycle in Natural Waters", Water Research, 6. 1259, 1972.

Furr, K, A. Lawrence, S. S. C. Tong, M. C. Grandolfo, R. A. Hofstader, A. Bach, W. H. Gutenmann, and D. J. Lisk, "Multielement and Chlorinated Hydrocarbon Analysis of Municipal Sewage Sludges of American Cities", Environmental Science and Technology, 10, 683, 1976.

Gulbrandsen, R. A., "Chemical Composition of Phosphorites of the Phosphoria Formation", Geochimica et Cosmochimica Acta, 30, 769, 1966.

Holt, B. R., and J. W. Moberly, "Environmental Mass Balance of Arsenic", Stanford Research Institute, 1976.

Hughes, E. E., E., M. Dickson, and R. A. Schmidt, "Control of Environmental Impacts from Advanced Energy Sources", U.S. Environmental Protection Agency, EPA 600/2-74-002,1074.

Judson, S., "Erosion of the Land", American Scientist, 56, 356, 1968.

Kessler, T., A. G. Sharrey, and R. A. Griedel, "Analysis of Trace Elements in Coal by Spark Source Mass Spectrometry", U.S. Bureau of Mines, RI 7714, 1972.

Klein, D. H., A. W. Anders, J. A. Carter, J. F. Emery, C. Feldman, W. Fulkerson, W. S. Lyon, J. L. Ogle, U. Talmi, R. I. Van Hook, and N. Bolton, "Pathways of Thirty-Seven Trace Elements Through a Coal-Fired Power Plant", Environmental Science and Technology, 9: 973-979, 1975.

Koh, S., "Extractive Metallurgy of Kuoko", presented at the joint meeting of the MMIJ-AIME, Tokyo, May 24-27, 1972.

MacKey, P. J., McKerrow, G. C. and Terassoff, P., "Minor Elements in the Noranda Process", Paper presented at the 104th Annual AIME Meeting, New York, February 16-20, 1975.

Magee, E. M., H. F. Hall, and G. M. Baige, "Potential Pollutants in Fossil Fuels", U.S. Environmental Protection Agency, EPA R2-73-249, 1973.

NAS, Medical and Biological Effects of Environmental Pollutants: ARSENIC, National Academy of Sciences, Washington, D.C., 1977.

Natusch, D. F. S., J. R. Wallace, and C. A. Evans, "Toxic Trace Elements: Preferential Concentration in Respirable Particles", Science, 183: 202-4, January 1974.

Onishi, H., "Arsenic", in Handbook of Geochemistry, Wedepohl, K. H. (ed.), Springer-Verlag, Berlin, 1969.

Onishi, H. and E. B. Sandell. "Geochemistry of Arsenic", Geochim. Cosmochi. Acta 7, 1, 1955.

Ruch, R. R., H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements", Environmental Geology Notes, No. 72, August 1974.

Schwitzgebel, K., R. T. Coleman, R. V. Collins, R. M. Mann, and C. M. Thompson, Trace Element Study at a Primary Copper Smelter, Vol I and II, U.S. Environmental Protection Agency, EPA-600/2-78-065a, 1978.

Slater, S. M., and R. R. Hall, "Electricity Generation by Utilities: 1974 Nationwide Emissions Estimates", AICHE Symposium Series 73, 291, 1977.

Stow, S. H., "The Occurrence of Arsenic and Color Causing Components in Florida Land-Pebble Phosphate Rock", Economic Geology 64, 667, 1969.

Sullivan, R. J., "Air Pollution Aspects of Arsenic and its Compounds", Litton Systems, Inc., PB 188 071, 1969.

Suta, Benjamin E., "Human Exposures to Atmospheric Arsenic", U.S. Environmental Protection Agency, September 1978.

Taylor, S. R., "Abundance of Chemical Elements in the Continental Crust: A New Table", Geochim. Cosmochim. Acta 28, 1273, 1968.

Union Carbide Corporation, "Review of the Environmental Effects of Arsenic", Oak Ridge National Laboratory, Oak Ridge, Tennessee, ORNL/E15-79, 1976.

United Nations, "Survey of World Iron Ore Resources", United Nations Department of Economic and Social Affairs, New York, 1970.

Vinogradov, A. P., "Regularity of Distribution of Chemical Elements in the Earth's Crust", Geochemistry (Geokhimiya), 1, 1956.